

Observation of intermixing at the buried CdS/Cu(In,Ga)Se₂ thin film solar cell heterojunction

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A combination of x-ray emission spectroscopy and x-ray photoelectron spectroscopy using high brightness synchrotron radiation has been employed to investigate the electronic and chemical structure of the buried CdS/Cu(In,Ga)Se₂ interface, which is the active interface in highly efficient thin film solar cells. In contrast to the conventional model of an abrupt interface, intermixing processes involving the elements S, Se, and In have been identified. The results shed light on the electronic structure and interface formation processes of semiconductor heterojunctions and demonstrate a powerful tool for investigating buried interfaces in general. © 1999 American Institute of Physics. [S0003-6951(99)03910-8]

Thin film solar cells based on a CdS/Cu(In,Ga)Se₂ heterojunction are one of the most promising and efficient systems in their field. Photovoltaic conversion efficiencies up to 17.7% on a laboratory scale¹ and up to 11.8% for full size modules (1.2 kW) have been achieved,² and the use of standard industrial thin film deposition techniques makes this system a cost-effective candidate as well. Despite the importance of the Cu(In,Ga)Se₂ (CIGS) based solar cell,³ however, the microscopic mechanism of how the photon-excited charge carriers are separated and transported to the electrodes is far from being fully understood. All existing models explaining the electronic properties of the heterojunction are based on an abrupt interface between the CdS buffer layer and the CIGS absorber material. In contrast, it is the purpose of this letter to demonstrate a nondestructive and atom-

specific way to determine that the buried interface is clearly nonabrupt with a graded distribution of S, Se, and In across the heterojunction.

We present data obtained by a combination of photoelectron spectroscopy (PES) and x-ray emission spectroscopy (XES) at beamline 8.0 of the Advanced Light Source.^{4,5} These techniques are both atom specific and sensitive to the electronic structure, and their combination enables us to derive information from a large range of experimental probing depths. Samples with different CdS overlayer thicknesses were prepared by rapid thermal processing (RTP) of elemental Cu, In, Ga, and Se layers on a Mo-coated Na-lime glass⁶ and by chemical bath deposition (CBD) of CdS, with both techniques being identical to the large-scale industrial approach.

Originally, it was envisioned by some that the interface between p-type CIGS and n-type CdS is the p-n junction responsible for the charge carrier creation and separation necessary to produce a solar cell current.⁷ However, PES experiments suggest that for evaporated CdS on a single-

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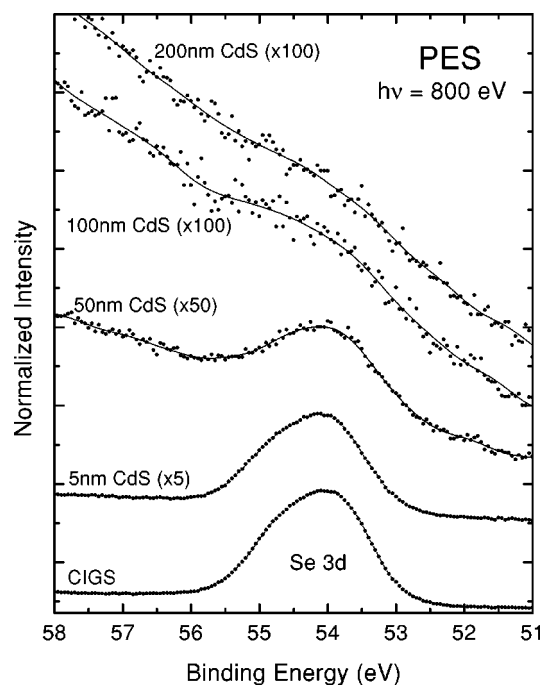


FIG. 1. Photoemission spectra of the Se 3d core levels for various CdS film thicknesses on Cu(In, Ga)Se₂, normalized by the exciting x-ray beam intensity, scaled as indicated, and offset along the intensity axis.

crystal CuInSe₂ substrate, a +0.6 eV (upward) conduction band barrier exists.⁸ Moreover, Schmid *et al.* suggest that the actual p-n junction in the thin film solar cell is formed within the CIGS absorber between an n-type ordered defect compound at the CIGS surface and the CIGS bulk, and they derive an essentially flat conduction band between CIGS and CdS.⁹ Note that, with PES, only the valence band offset can be determined, and a conduction band offset has to be calculated by assuming appropriate band gaps. Also, the previous results were obtained with *evaporated* CdS. An indirect determination of the CBD CdS/CIGS band offset also derives an essentially flat conduction band across the junction, but again appropriate band gaps have to be assumed.¹⁰

In the case of a graded junction (as will be demonstrated here for CBD CdS) the assumption of uniform band gap values for the heterojunction partners is incorrect. For example, by forming CdS_{1-x}Se_x instead of CdS in the overlayer, the band gap can be decreased from 2.4 eV for $x=0$ to 1.8 eV for $x=1$.¹¹ Similarly, the band gap of CuInSe₂ (1.1 eV) is increased by forming CuInS_ySe_{2-y}, with a maximum gap of 1.5 eV for $y=2$. With CBD being the preferred technique to deposit CdS for CdS/CIGS-based solar cells, it is crucial to understand the chemical and electronic properties of the graded junction in order to understand the performance of the whole solar cell device. It should also be noted that in the case of CdS/CdTe solar cell intermixing is well accepted and believed to usually enhance the cell performance.¹²

During the formation of the CdS/CIGS interface Se and In diffuse into the CdS overlayer. For Se, this can be derived from the photoemission spectra of Fig. 1. A detailed discussion of the In diffusion will be presented elsewhere. A significant Se signal can be observed for samples with CdS thicknesses up to 50 nm, and a weak structure remains for even higher coverages. Note that the inelastic mean free path

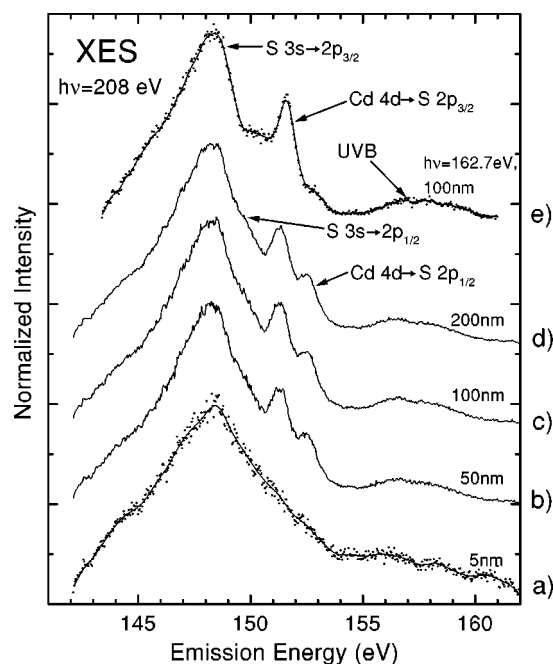


FIG. 2. X-ray emission spectra of the electronic transition between valence band states and ionized S 2p core levels, for various CdS thicknesses [(a)–(d), excitation energy $h\nu=208$ eV] and excited between the ionization thresholds of S 2p_{3/2} and S 2p_{1/2} (e, $h\nu=162.7$ eV).

of the electrons contributing to the Se 3d peak ($E_{\text{kin}}=746$ eV) is on the order of 1 nm, which makes PES a very surface sensitive probe. With such high surface sensitivity and with a simple attenuation model one would expect that the Se 3d PES signal for CIGS buried under a 5 nm CdS overlayer is attenuated by a factor of about 150. For a 50 nm overlayer, the expected attenuation factor is 10^{21} . In our experiments such a rapid attenuation is only observed for Cu emission (3d levels) from Cu atoms in the CIGS layer, and for Na impurities originating from the soda-lime glass substrate, which are identified to be localized at the CIGS surface.¹³ In contrast we find that the Se signals are attenuated much less. Because the CdS layer thickness commonly employed in CIGS based cells is about 15 nm, it is very likely that Se is present throughout the entire CdS film, presumably forming a sulfoselenide. As mentioned above, there is also evidence for In diffusion into the overlayer. However, an In photoemission signal could only be observed for CdS thicknesses of 5 and 15 nm, but not for 50 nm, indicating that the diffusion length for In is smaller than that for Se. It is therefore appropriate to distinguish two different regions within the overlayer: an interface-near region of the general form Cd_vIn_wS_{1-y}Se_y and a CdS_{1-z}Se_z region further away from the interface. Note that all stoichiometries will vary throughout the overlayer.

Analogous to a diffusion of Se into the overlayer, a simultaneous diffusion of S into the CIGS substrate is to be expected. We did in fact find direct spectroscopic evidence for such behavior in the x-ray emission spectra (XES), as shown in Fig. 2. In this experiment, the S 2p core levels are ionized and the x-ray emission due to electronic transitions from the valence band region into these core holes is monitored with an energy-dispersive detector. In particular, emission lines representing the S 3s→2p transitions, the

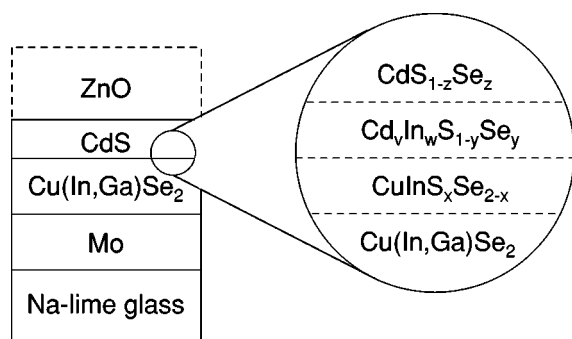


FIG. 3. Schematic diagram of the thin film CdS/Cu(In,Ga)Se₂ solar cell (left), showing the intermixing behavior at the buried photovoltaic interface (right). Layer thicknesses are not drawn to scale.

Cd 4d→S 2p transitions, and the Cd 5s→S 2p transition from the upper valence band (UVB), which is composed of S 3p, Cd 5s, and Cd 5p contributions, can be identified, as marked in Fig. 2, spectra (d) and (e). For a more detailed discussion of the CdS XES spectrum see Ref. 14. In spectrum (e) the exciting photon energy was tuned to 162.7 eV so that only the S 2p_{3/2} core level was ionized. Hence only the transitions involving the S 2p_{3/2} level are observed. The presence of a Cd-S crossover transition is an interesting finding in itself, because it demonstrates a wave function overlap between the S 2p and the Cd 4d orbitals. This indicates that the Cd 4d states are involved in the chemical bonding in CdS, analogous to the fact that Cd 4d levels in II-VI semiconductors show band dispersion and have to be included in band structure calculations.¹⁵

Spectra (a)–(d) in Fig. 2 were recorded for the same set of samples as in Fig. 1. For ease of comparison the spectra were multiplied by appropriate scale factors [(a): 28, (b): 2.7, (c): 1.9, and (d): 1]. While spectra (b)–(d) are essentially identical to each other and to the CdS reference spectra,¹⁴ this is not the case for the 5 nm CdS overlayer sample, for which the Cd 4d→S 2p transitions are almost entirely absent. Apparently, no overlap between the S 2p orbitals and the Cd 4d orbitals exists for a thin CdS overlayer, i.e., Cd and S atoms do not form the usual Cd-S bond, but are most probably separated. This is interpreted as the formation of an additional sulfoselenide, namely CuInS_xSe_{2-x}, at and below the surface of the CIGS substrate. In addition, a chemical bond between In and S such as in In₂S₃ seems possible, both within the CIGS substrate and the CdS overlayer. Independent of the details of the interpretation, the experimental data clearly demonstrate that the chemical and atomic configuration of the S atoms is completely different from what one would expect for an abrupt CdS/CIGS interface.

The experimental findings and their interpretation are summarized in a schematic block diagram of the entire CdS/CIGS-based solar cell (Fig. 3). On the right hand side of the diagram the various regions of intermixing are depicted. Our results suggest a graded interface structure, with a transition from the Cu(In,Ga)Se₂ substrate, through CuInS_xSe_{2-x} and Cd_vIn_wS_{1-y}Se_y interlayers, towards a CdS_{1-z}Se_z layer, and finally, for thick CdS, to a pure CdS overlayer. All stoichiometries are expected to vary throughout these layers. Within the range of commonly employed overlayer thick-

nesses (<50 nm) our experiments provided no evidence for a pure CdS layer at any sample depth.

These findings show that the idea of an abrupt CdS/CIGS interface is incorrect, at least for the technologically relevant case of chemical bath deposition of CdS on Cu(In,Ga)Se₂ thin films manufactured by rapid thermal processing. Previous conduction band offset analyses will have to be reinterpreted in light of a significantly more complex buried interface. Moreover, we have demonstrated that a combination of two x-ray based techniques (photoelectron spectroscopy and x-ray emission spectroscopy) constitutes a powerful tool to investigate the atom-specific structure of buried interfaces and their intermixing behavior.

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